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MEMORANDUM FOR PRS (In-House/Contractor Publication)

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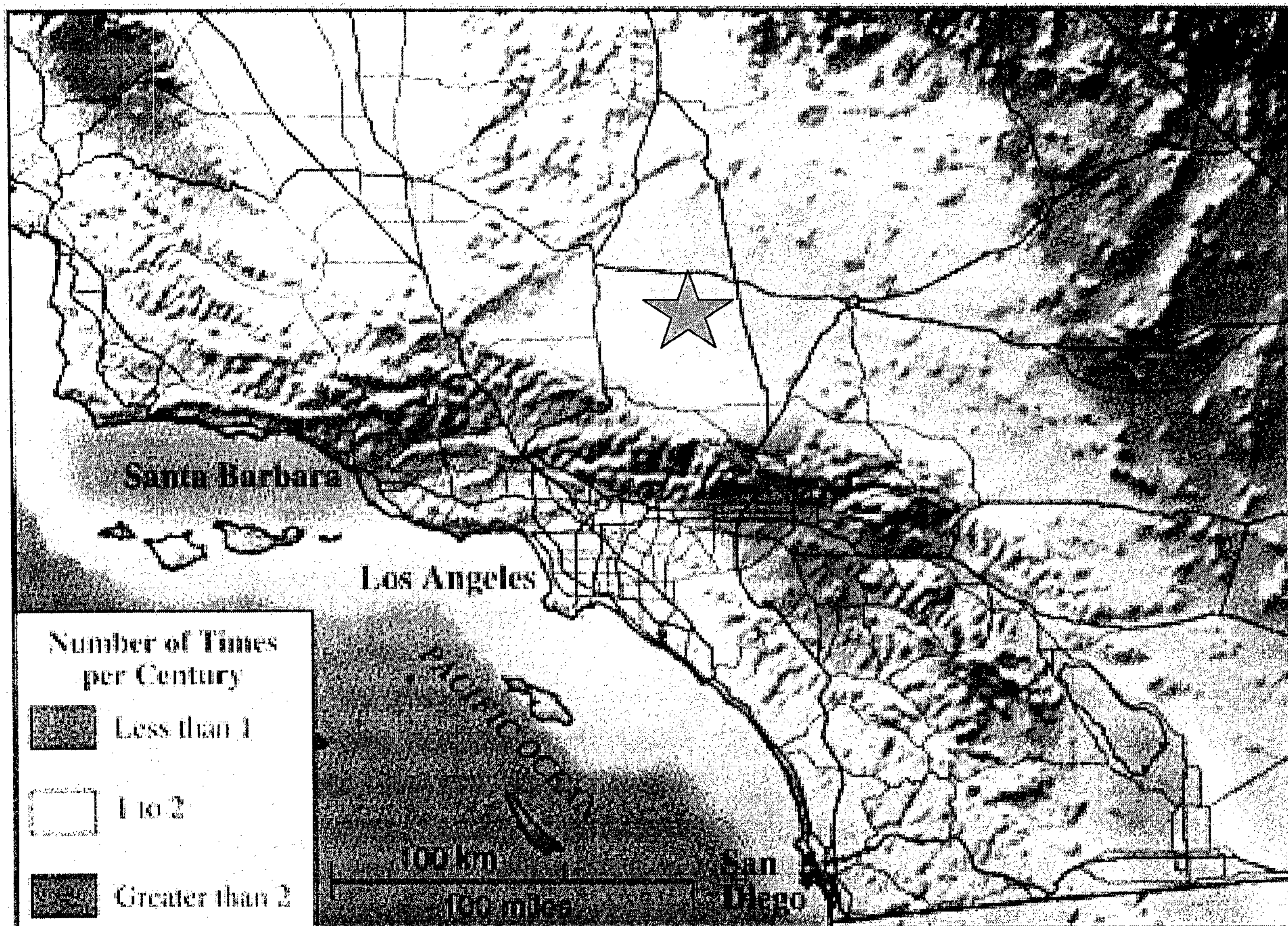
SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2003-048**
Timothy S. Haddad and Capt. Rene Gonzalez "Organic Polymers Modified with Inorganic Polyhedra"

American Chemical Society Conference **(Statement A)**
(New Orleans, LA, 23-27 Mar 2003) **(<u>Deadline: 21 Mar 2003</u>)**

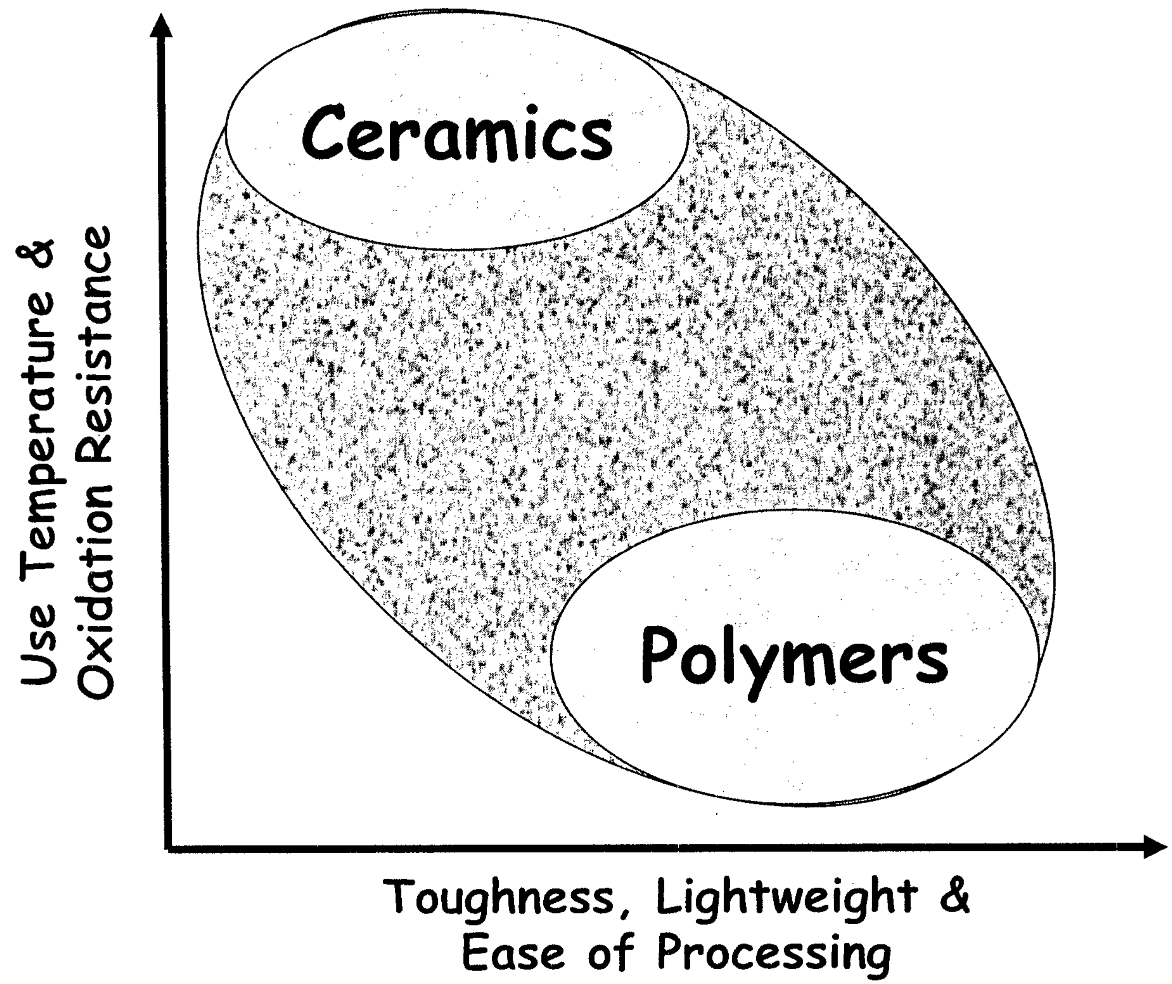
ORGANIC POLYMERS MODIFIED WITH INORGANIC POLYHEDRA

Tim Haddad and Rene Gonzalez
ERC Inc., Air Force Research Lab

Edwards Air Force Base, CA



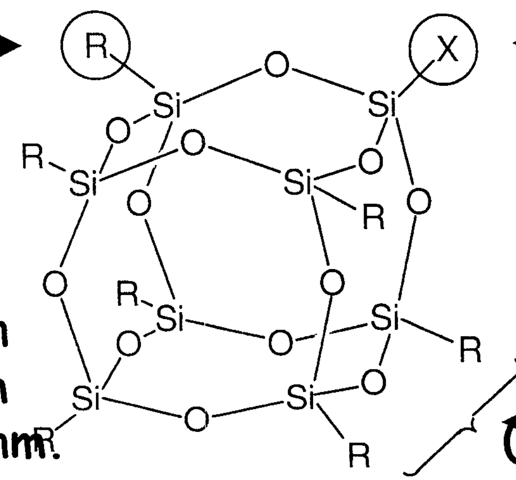
Hybrid Inorganic/Organic Polymers



- Hybrid plastics bridge the differences between ceramics and polymers

Anatomy of a Polyhedral Oligomeric Silsesquioxane (POSS) Macromer

Nonreactive organic (R) groups for solubilization and compatibilization.



May possess one or more functional groups suitable for polymerization or grafting.

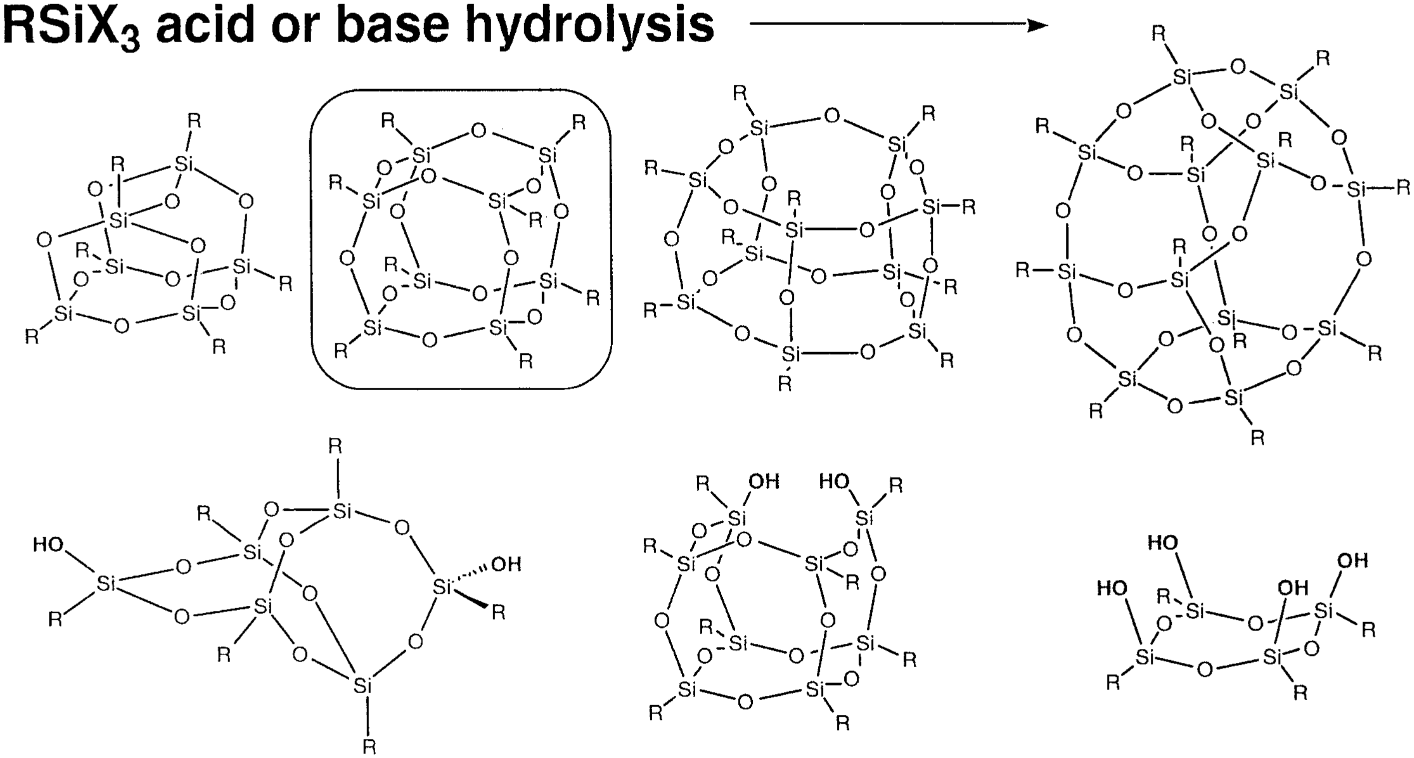
Nanoscopic in size with an Si-Si distance of 0.5 nm and a R-R distance of 1.5 nm.

Thermally and chemically robust hybrid (organic-inorganic) framework.

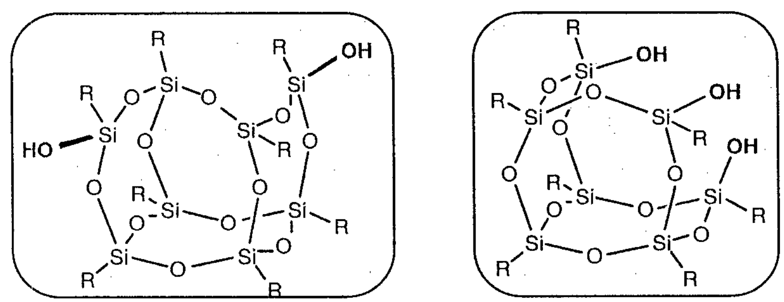
Precise three-dimensional structure for molecular level reinforcement of polymer segments and coils.

POSS Synthesis

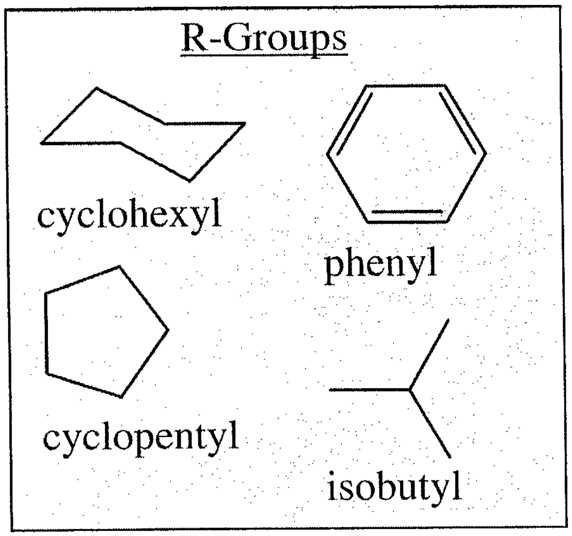
$RSiX_3$ acid or base hydrolysis

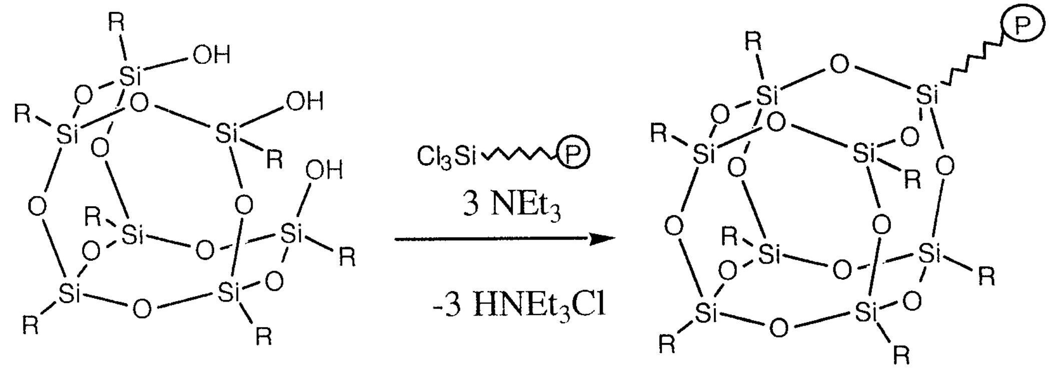


Brown & Vogt: *JACS*, 1965, 4313
Feher et al: *JACS*, 1989, 1741;
Organometallics, 1991, 2526;
Chem Comm, 1999, 1705, 2309



POSS Macromers For Nanocomposites



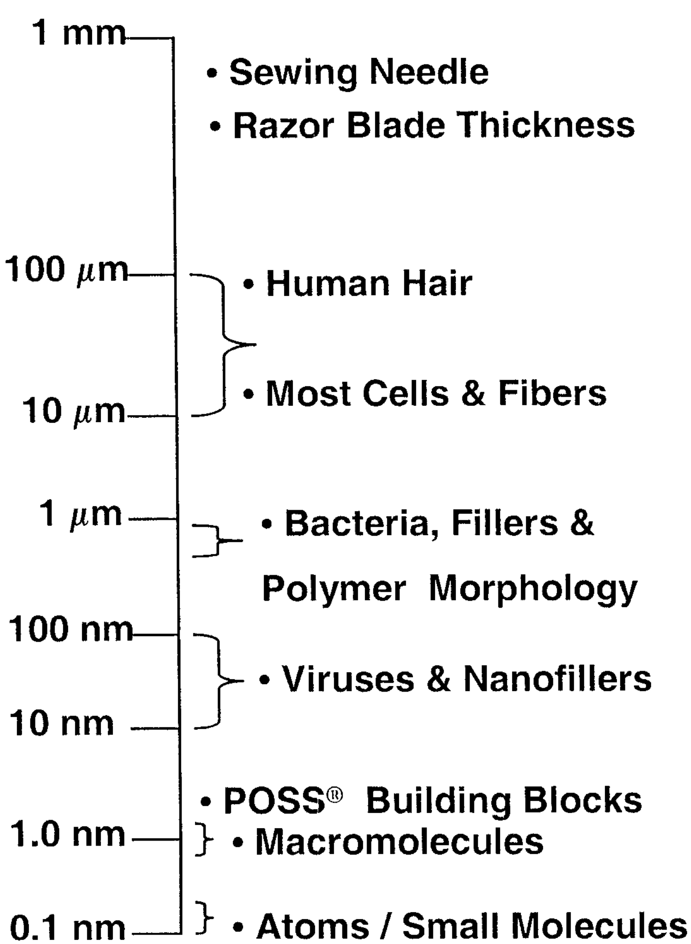


Halides	Nitriles	Silanes	Styryls
Alcohols	Amines	Silanols	a-olefins
Esters	Isocyanates	Silylchlorides	Acrylics
Bisphenols	Epoxides		Norbornenyls

POSS-based macromers are available through either **Geleste** or **Aldrich**

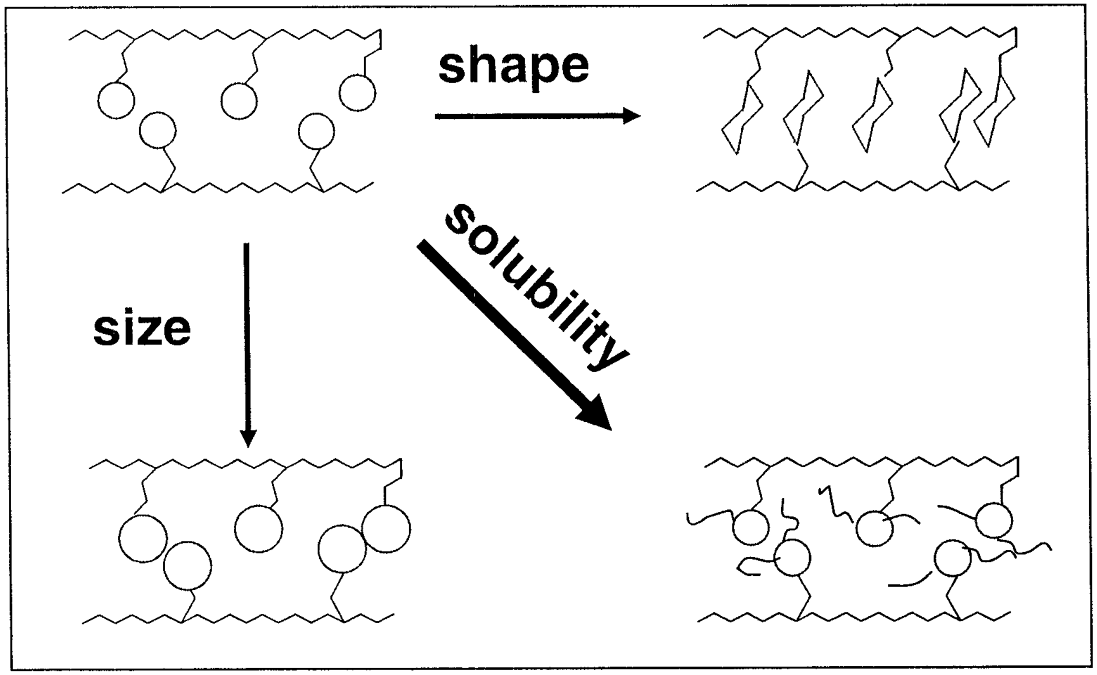
POSS technology is commercialized by **Hybrid Plastics** in Fountain Valley CA

Why POSS and Why Nano?



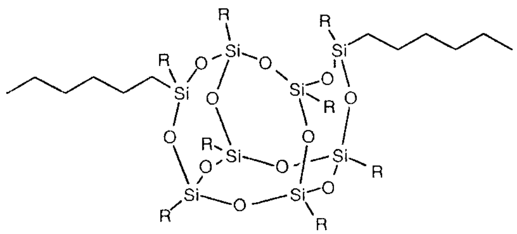
Field	Property	Critical Length
Electronics	Tunneling	1-100 nm
Optical	Quantum Well	1-100 nm
	Wave Decay	10-1000 nm
Polymers	Primary Structure	0.1-10 nm
	Secondary Structure	10-1000 nm
Mechanics	Dislocation Interaction	1-1000 nm
	Crack Tip Radius	1-100 nm
	Entanglement Rad.	10-50 nm
Therm-Mech.	Chain Motion	0.5-50 nm
Nucleation	Defect	0.1-10 nm
	Critical Nucleus Size	1-10 nm
	Surface Corrugation	1-10 nm
Catalysis	Surface Topology	1-10 nm
Biology	Cell Walls	1-100 nm
Membranes	Porosity Control	0.1-5 nm

Structure-Property Relationships

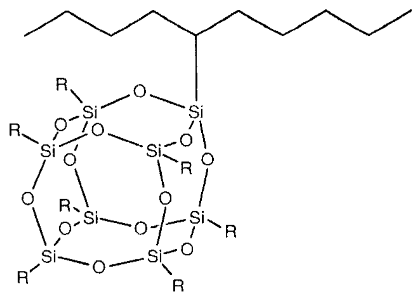


- Maximizing property enhancements through changes at the nano level
- Polymer miscibility vs. POSS/POSS interactions

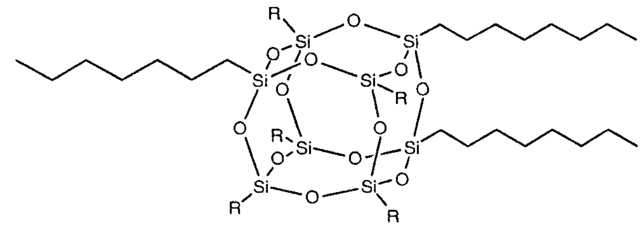
POSS Polymer Incorporation



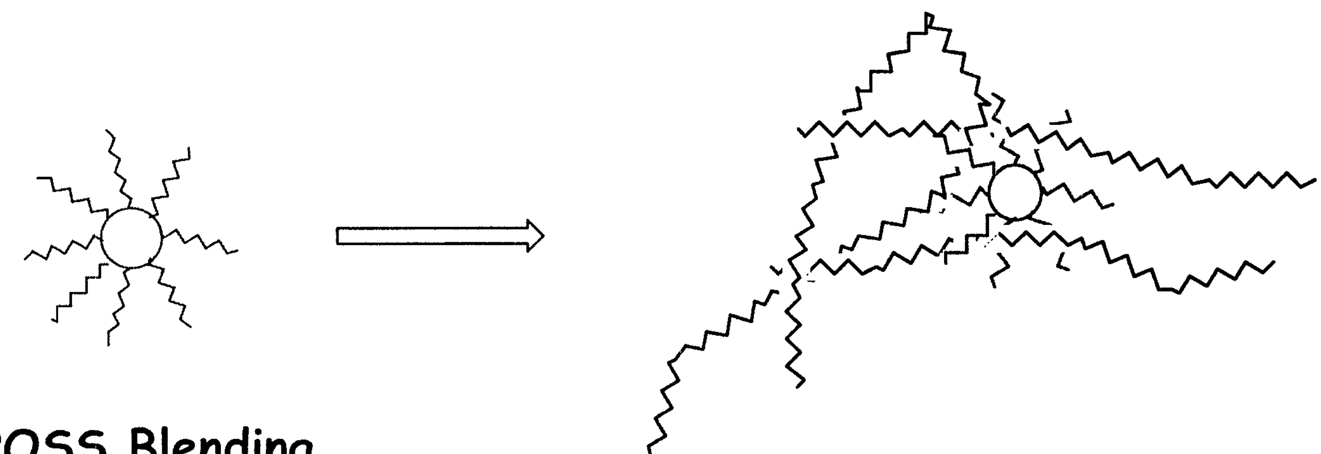
POSS Bead



POSS Pendant



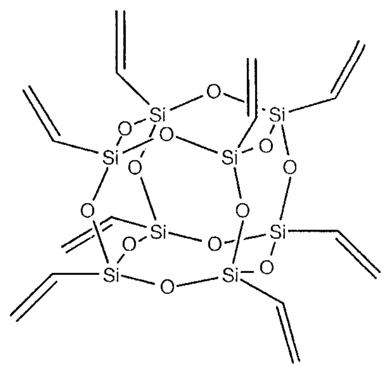
POSS Crosslinking



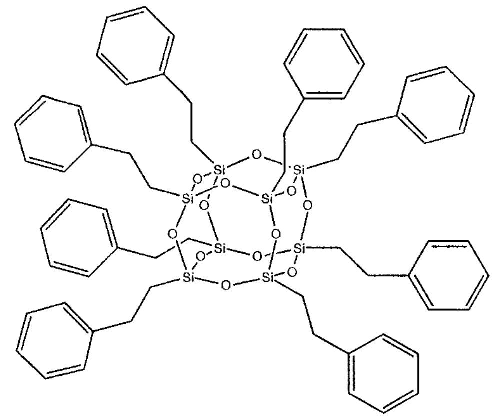
POSS Blending

Size & Shape

50 Wt % POSS Blends in 2 Million MW PS

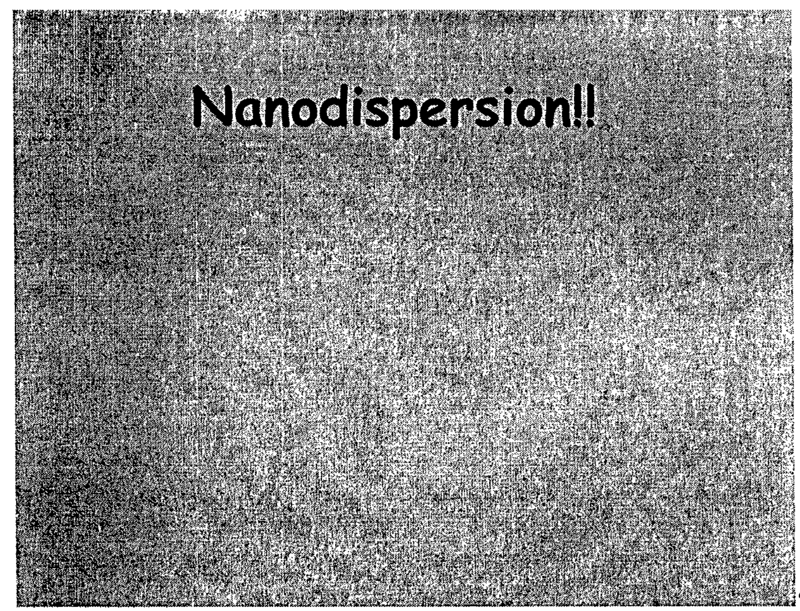


Vi_8T_8

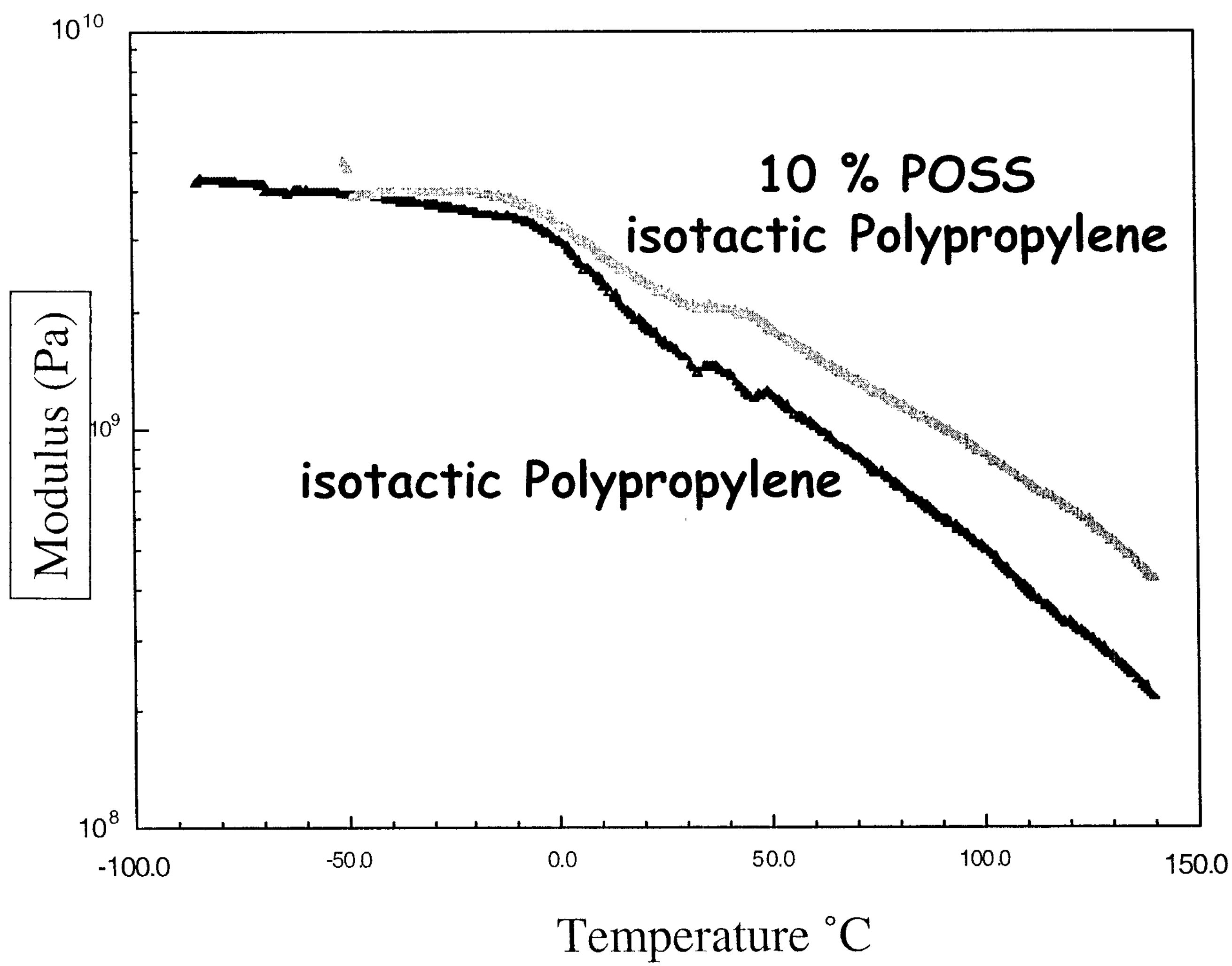


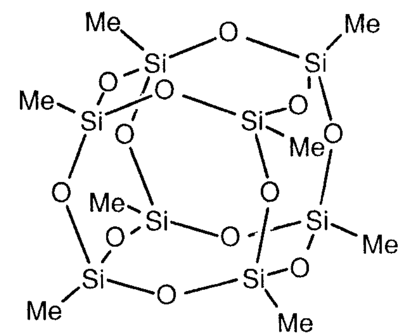
$Phenethyl_8T_8$

1 μm



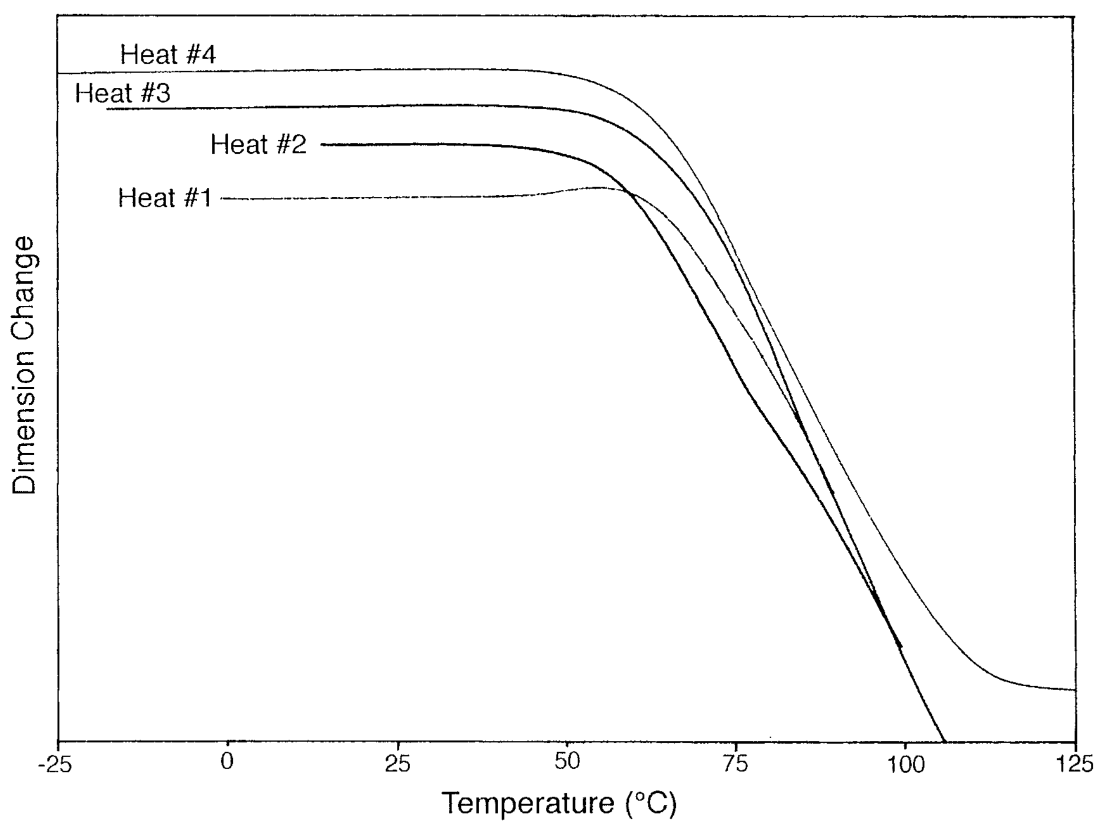
DMA of 10 Wt % POSS in isotactic Polypropylene

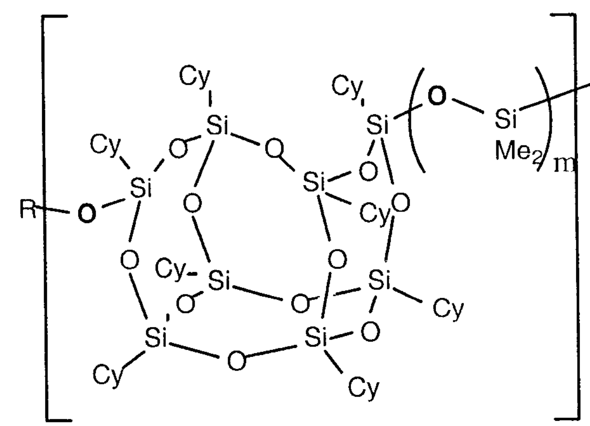




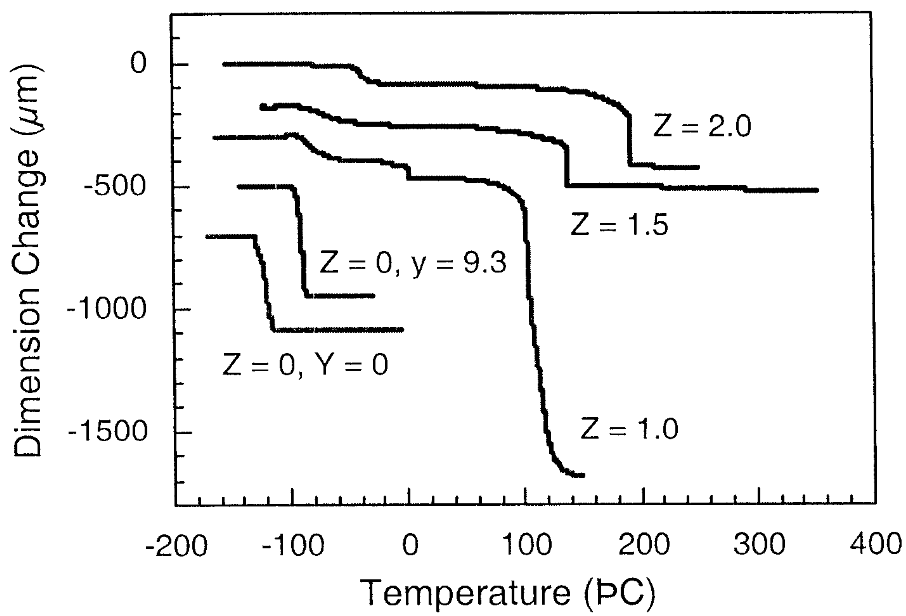
PDMS-POSS TMA Characterization

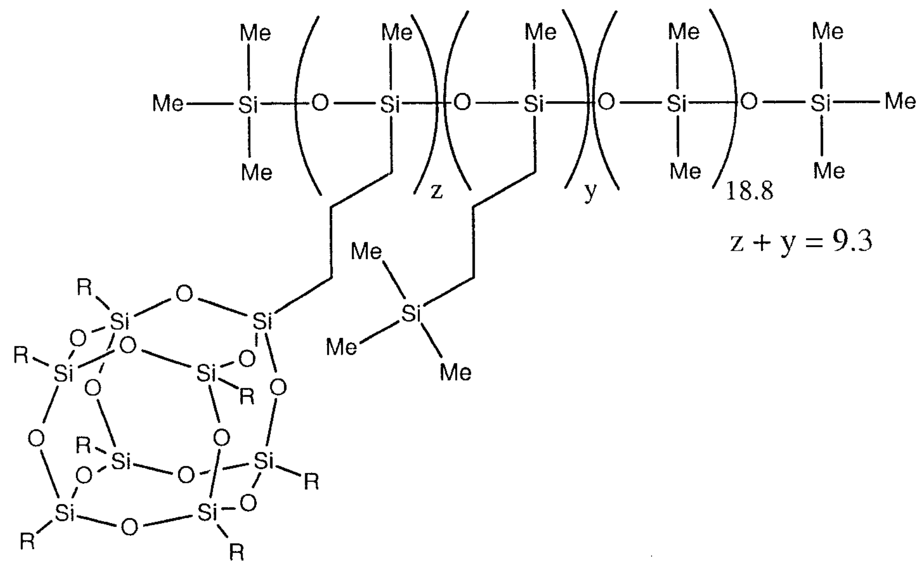
The POSS/Siloxane copolymers with four or more Si-O repeat units in the siloxane segment have softening temperatures well below the decomposition temperatures.





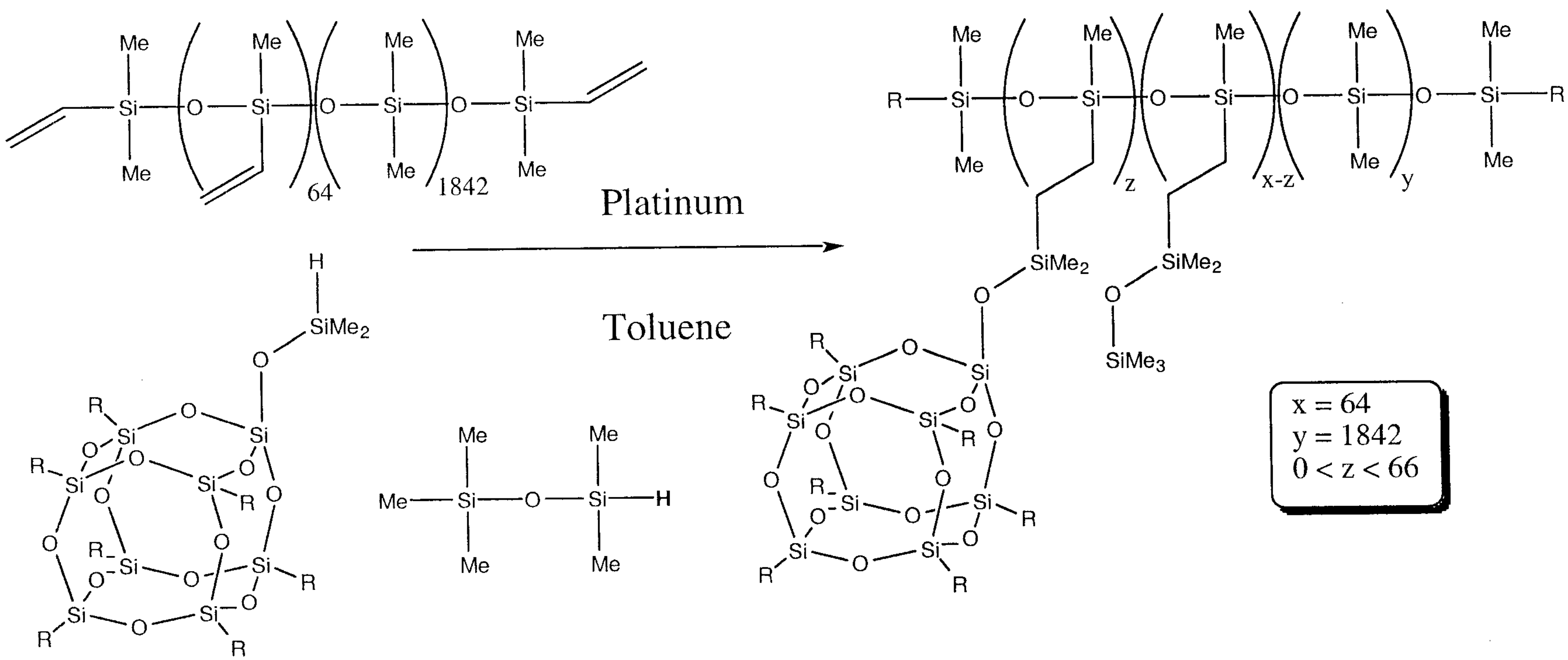
TMA of Pendent POSS-Siloxanes





z + y = 9.3

Hydrosilation to High MW PDMS

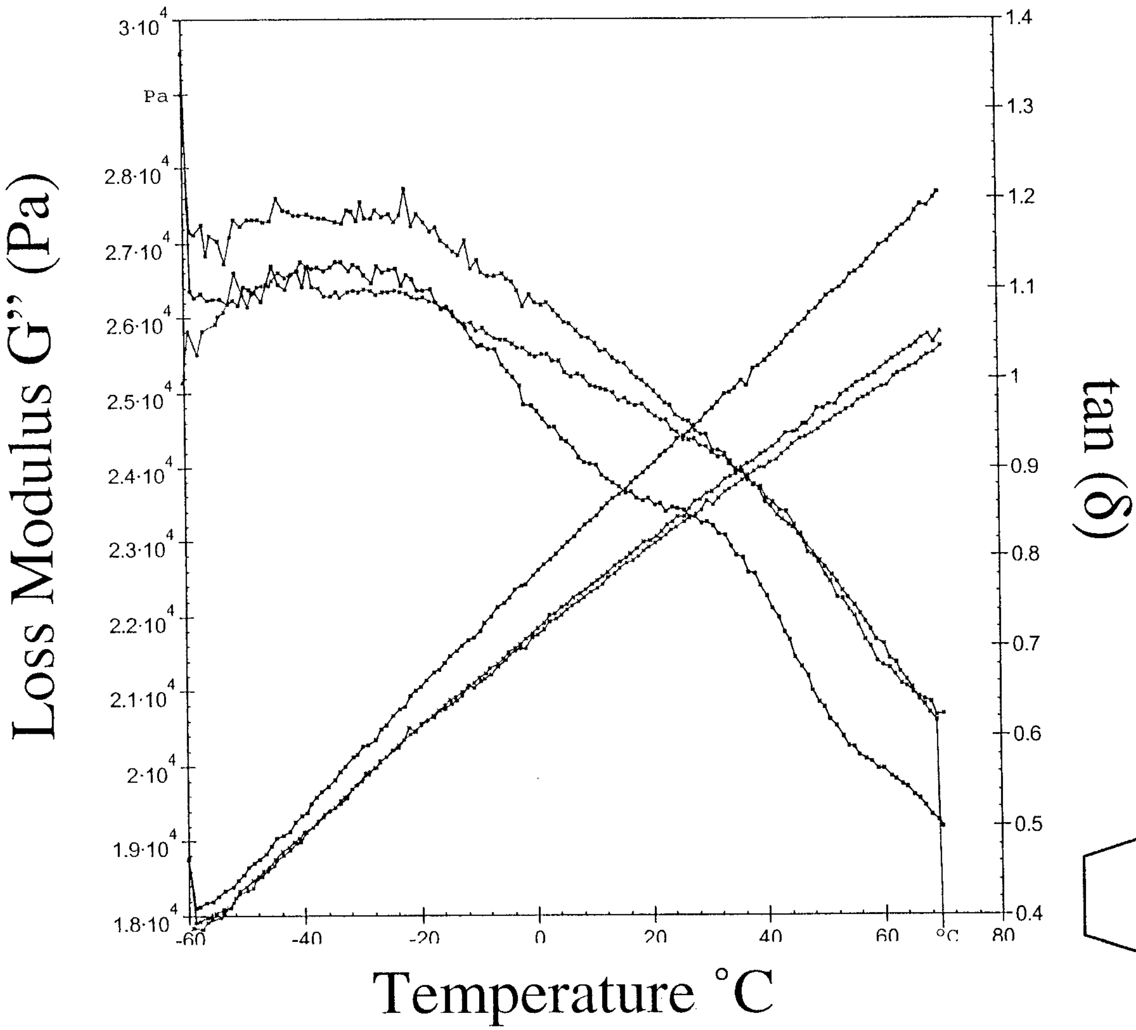


$x = 64$
$y = 1842$
$0 < z < 66$

Used 5 weight % POSS

There are about 7 POSS-macromers per PDMS chain

Comparison of Three T8-POSS Macromers

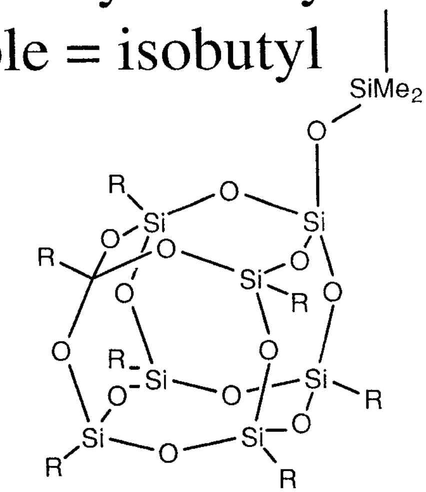


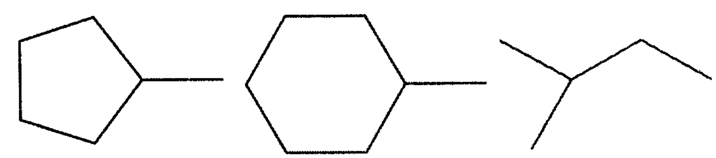
PDMS + 5 wt % POSS

Blue = cyclopentyl

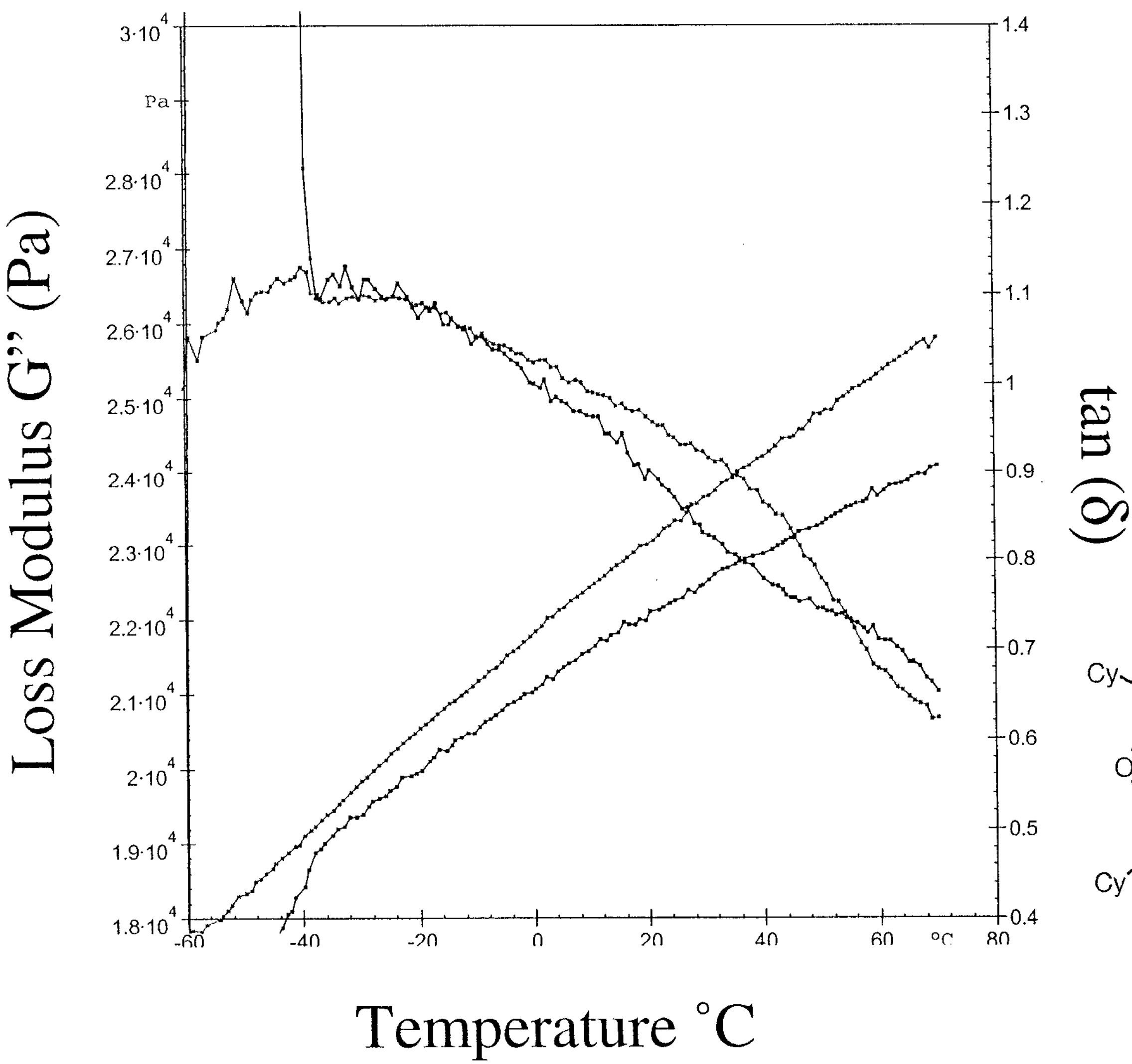
Red = cyclohexyl

Purple = isobutyl

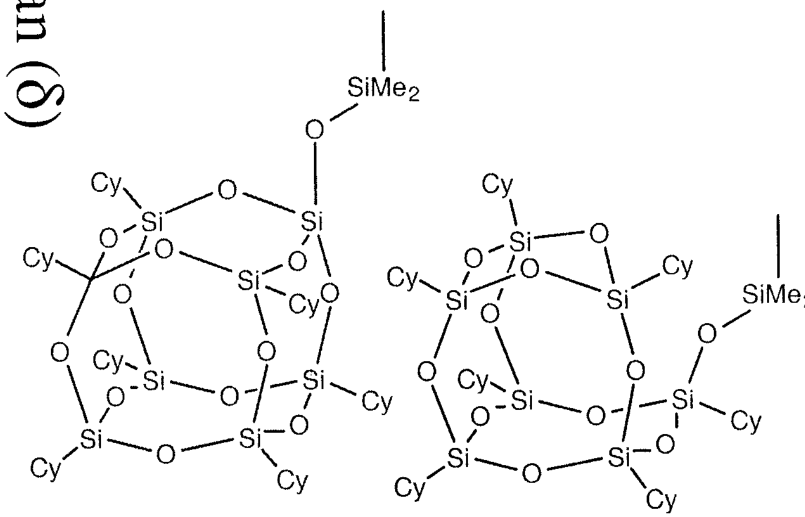




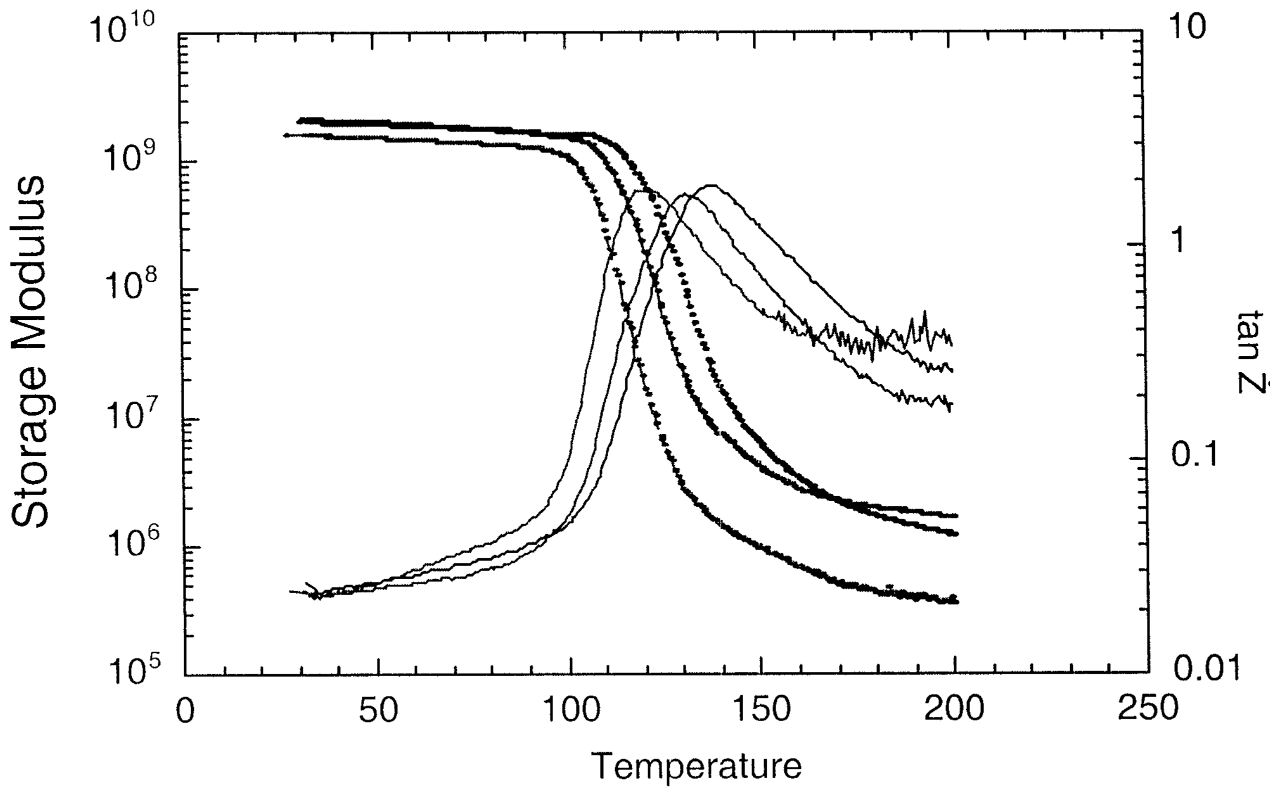
Comparison of Two POSS Polyhedra

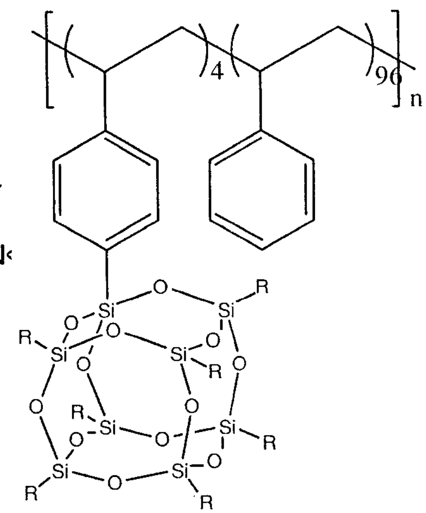


PDMS + 5 wt %
CyclohexylPOSS
Red = T8-POSS
Blue = T7-POSS



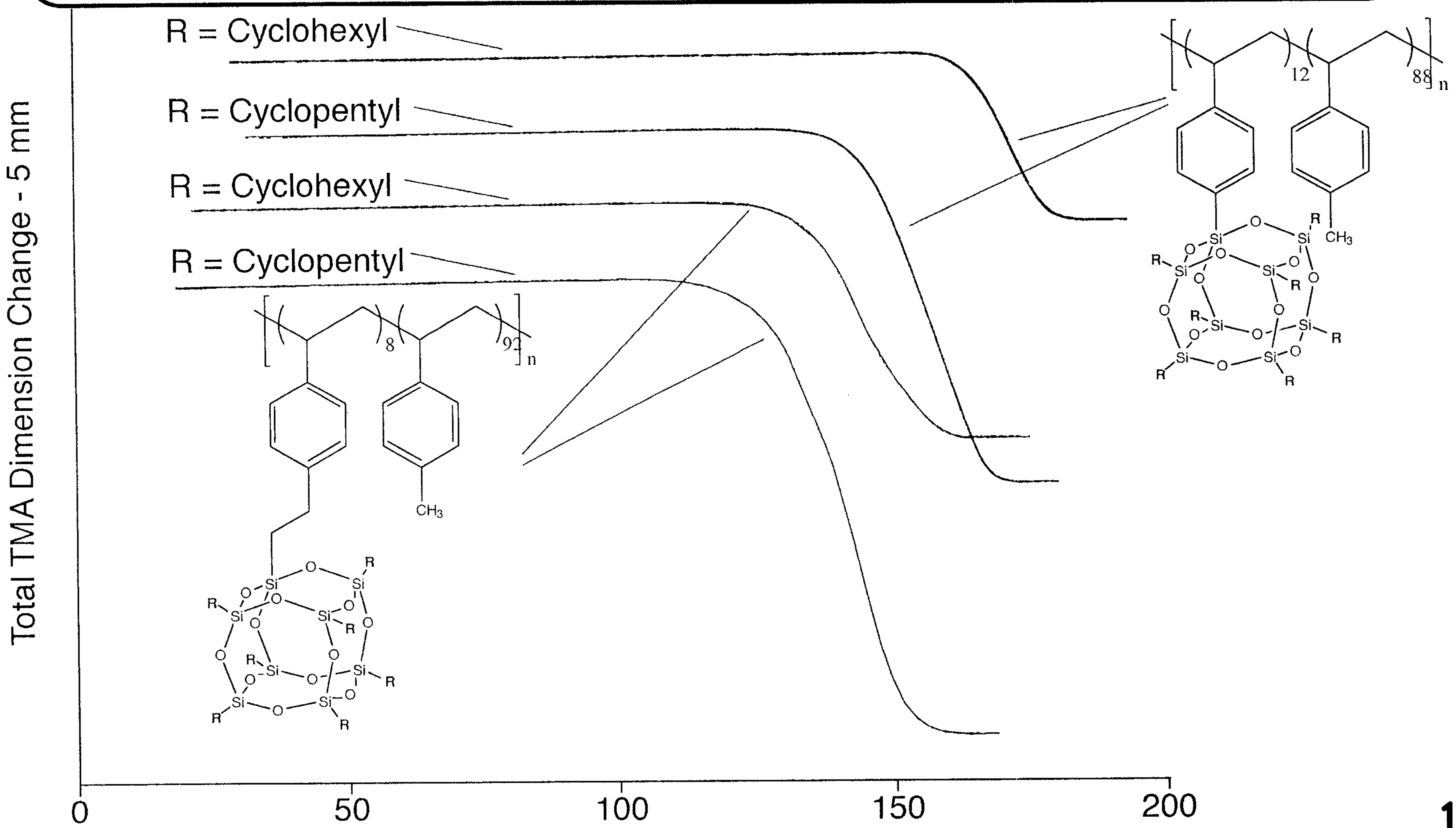
DMA of 30 wt % POSS Polystyrenes



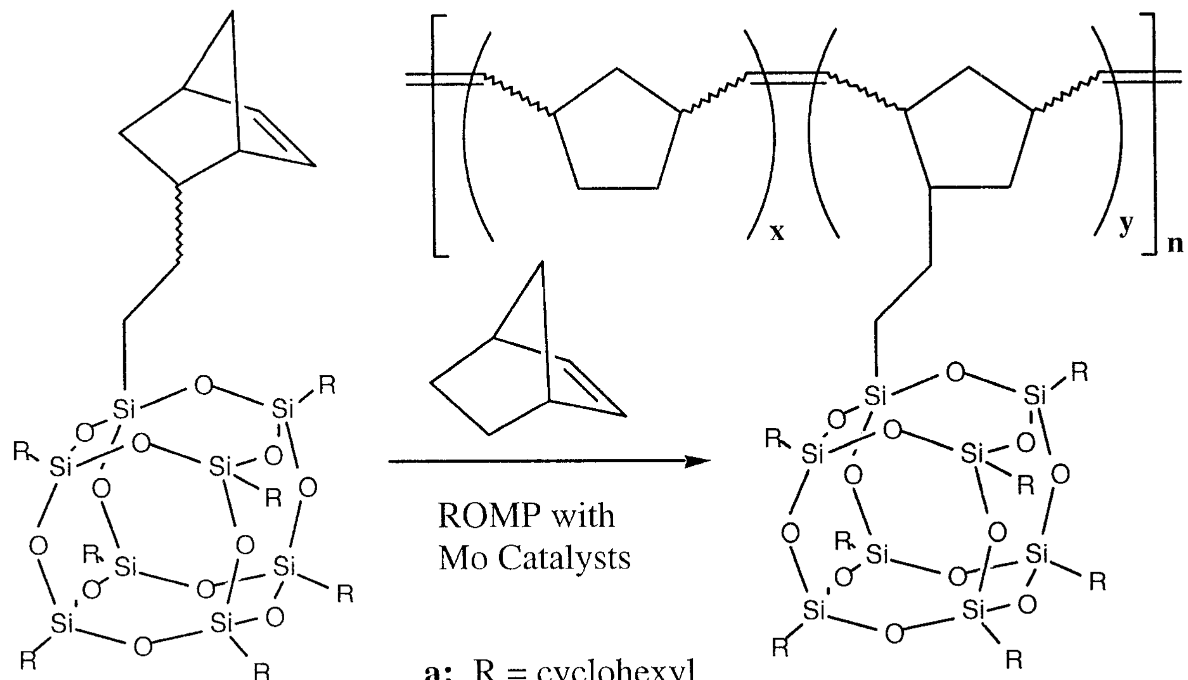


- Comparison of isobutyl, cyclopentyl & cyclohexyl
- Bulk polymerized samples

TMA Plot Comparison For POSS-Styryl and POSS-EthylStyryl Polymers (R = Cyclohexyl and Cyclopentyl)



Polymerization of POSS Norbornenes



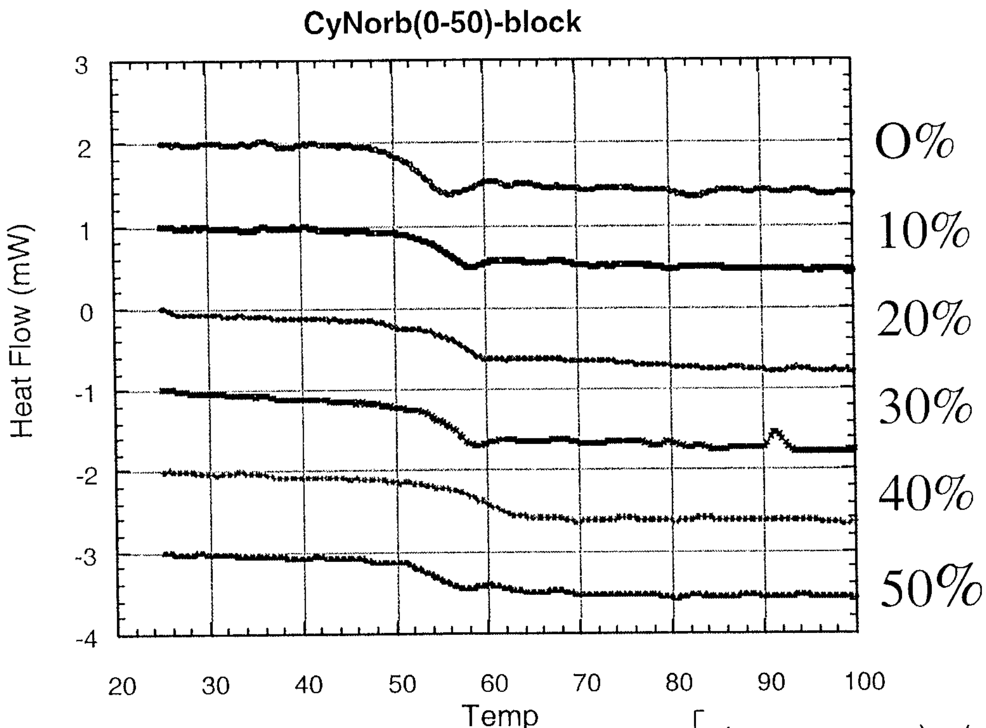
6a,b

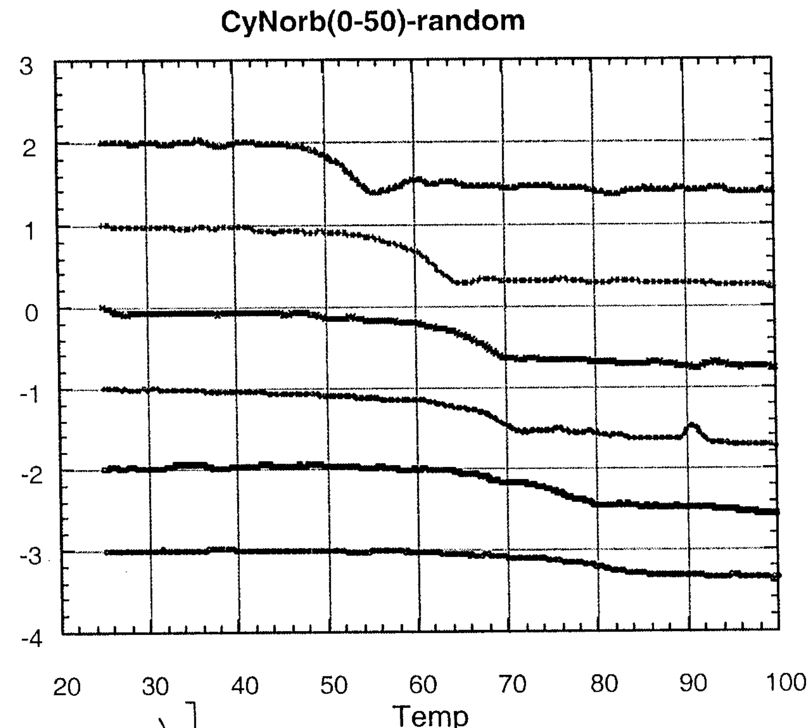
a: R = cyclohexyl
b: R = cyclopentyl

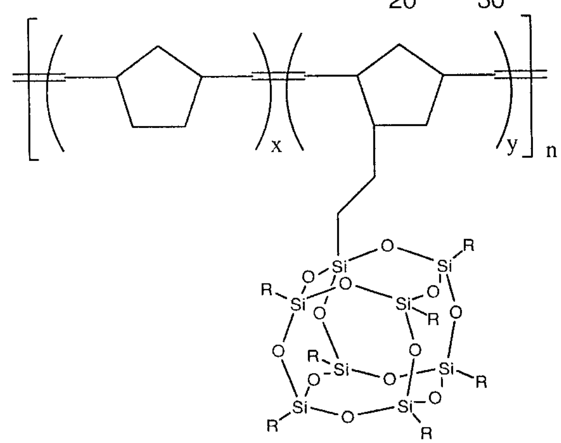
7a,b

Both block and random copolymers were synthesized.
The wt. % POSS was varied from 0 to 50 wt. % POSS.

DSC Data for POSS-Norbornenes

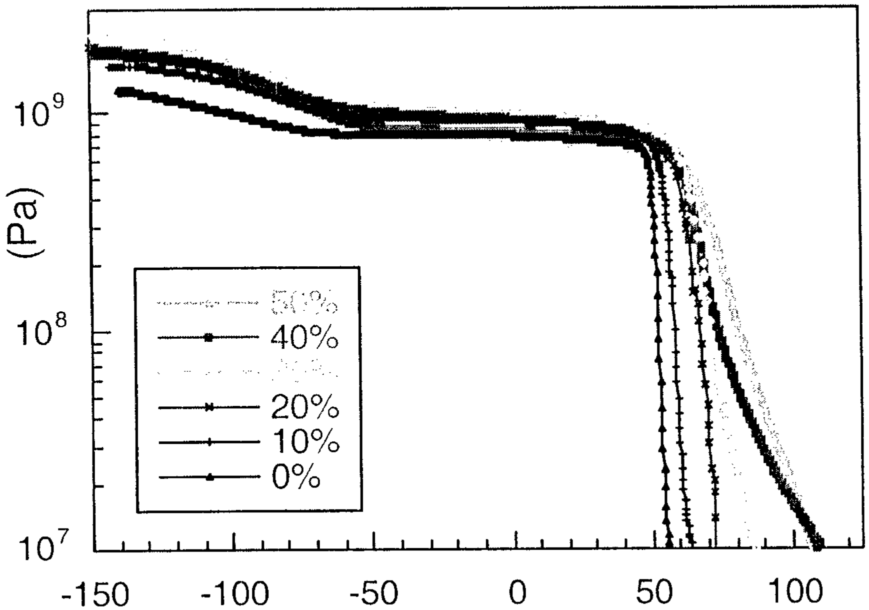


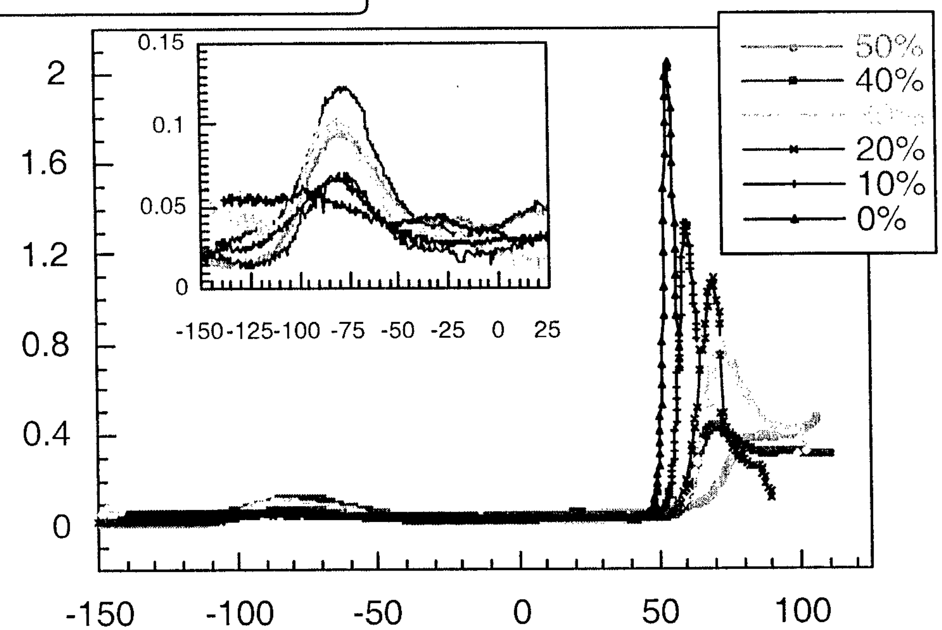


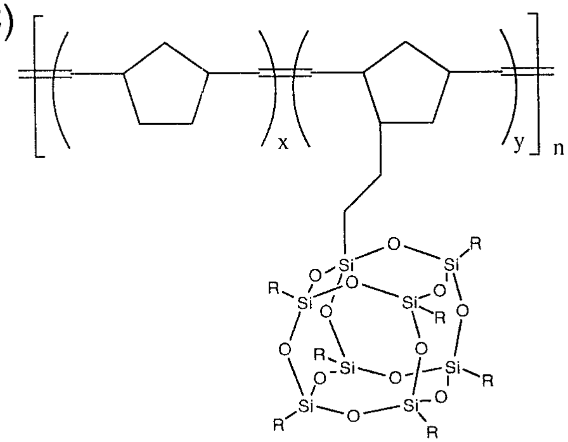


Storage Modulus and Loss Tangent

Cyclohexyl Relaxation: 14.7 kcal/mol





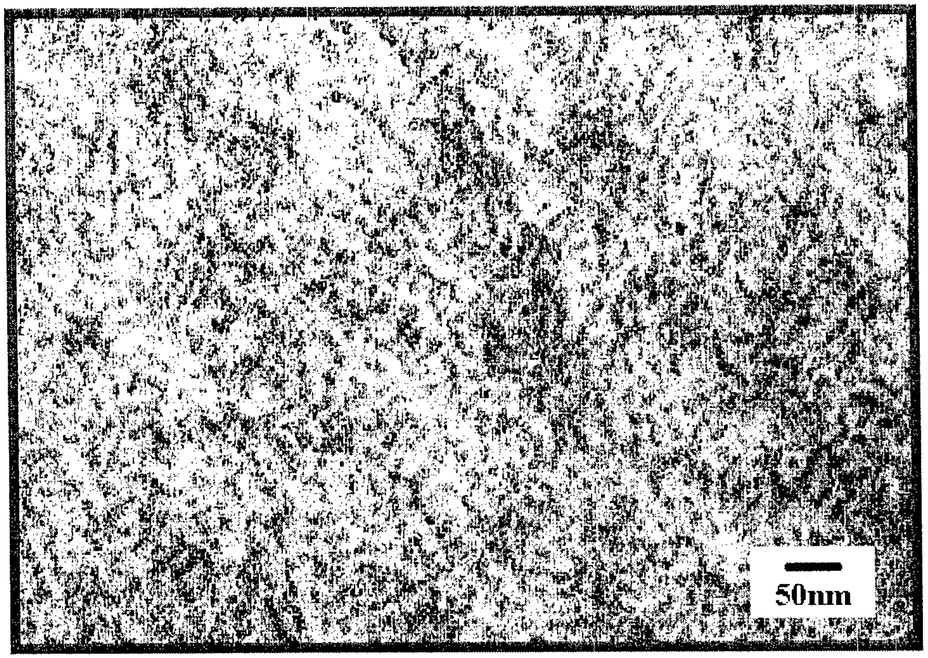


No Maximum for 50% CyPOSS

Various Wt % Cyclohexyl POSS Polynorbornene Random Copolymers

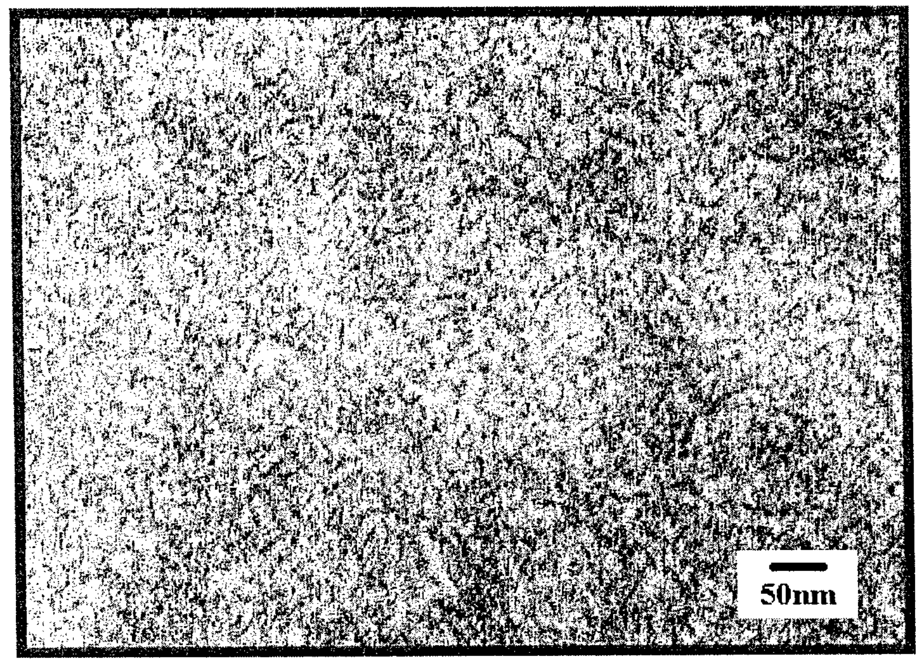
TEM of Random POSS Norbornenes

50CyPOSS/PN



"Coarse" Cylinder Nanostructure
(Diameter ~ 12nm)

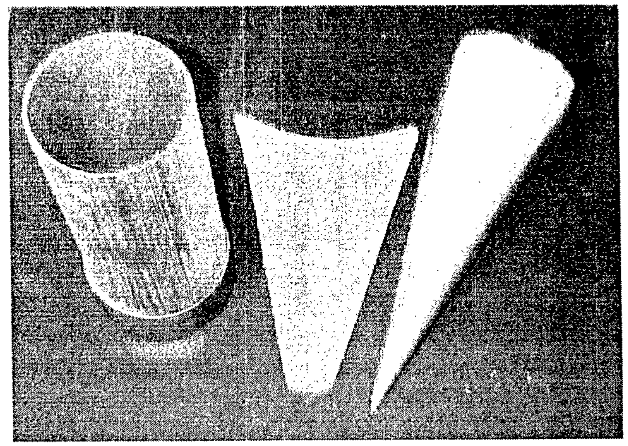
50CpPOSS/PN



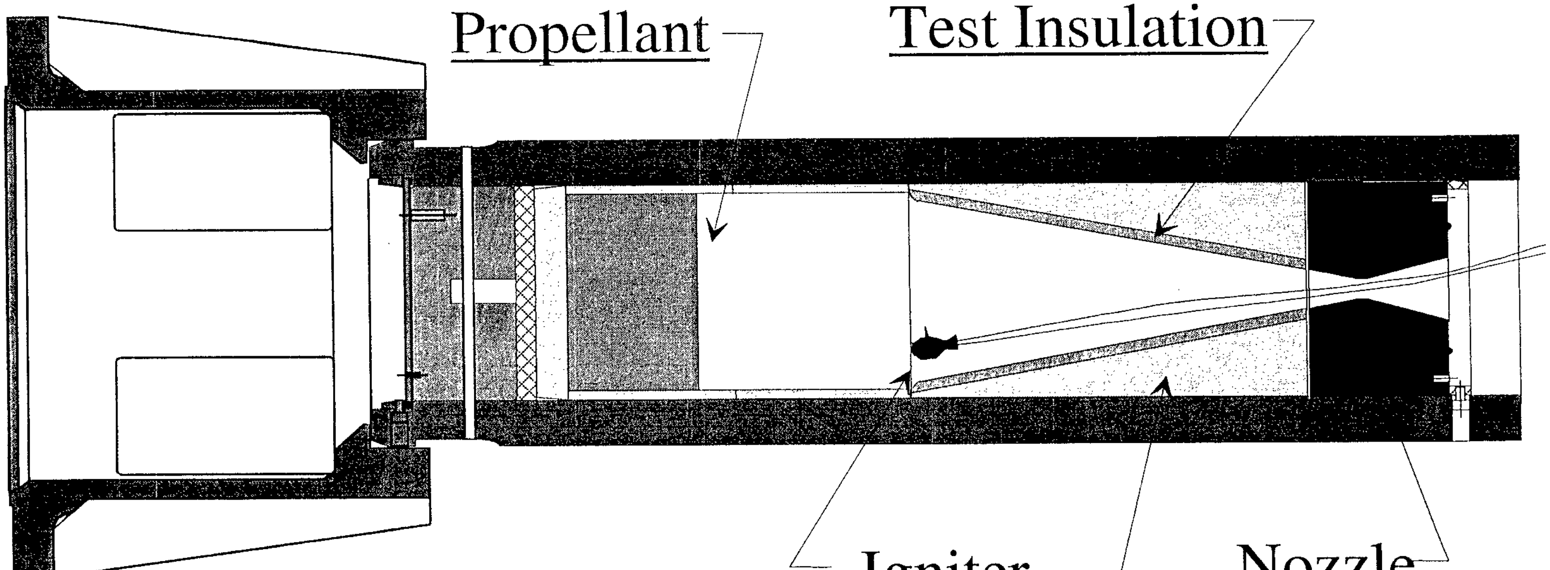
"Fine" Cylinder Nanostructure
(Diameter ~ 6nm)

CyclohexylPOSS-rich domains may entrain more unoriented polynorbornene chains than CyclopentylPOSS-rich domains.

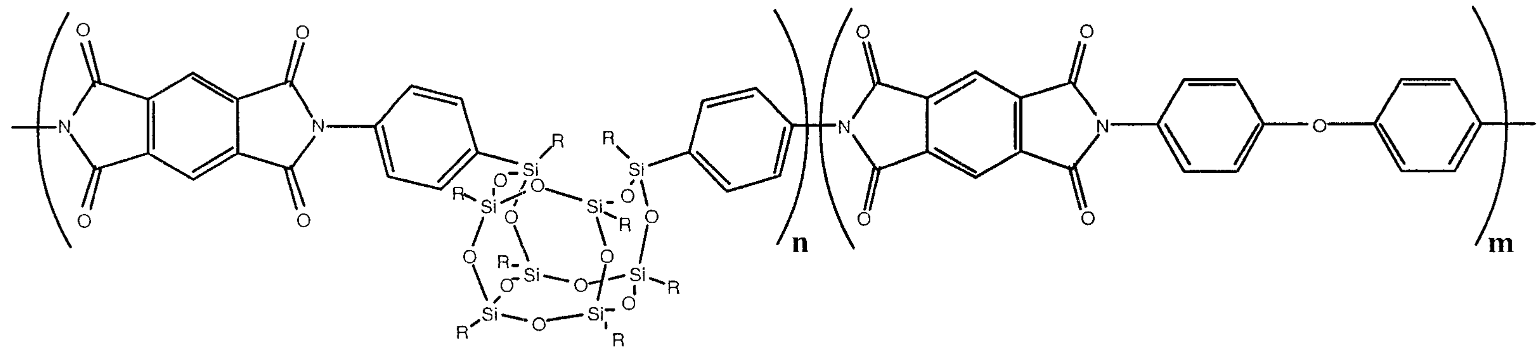
Solid Rocket Motor Insulation



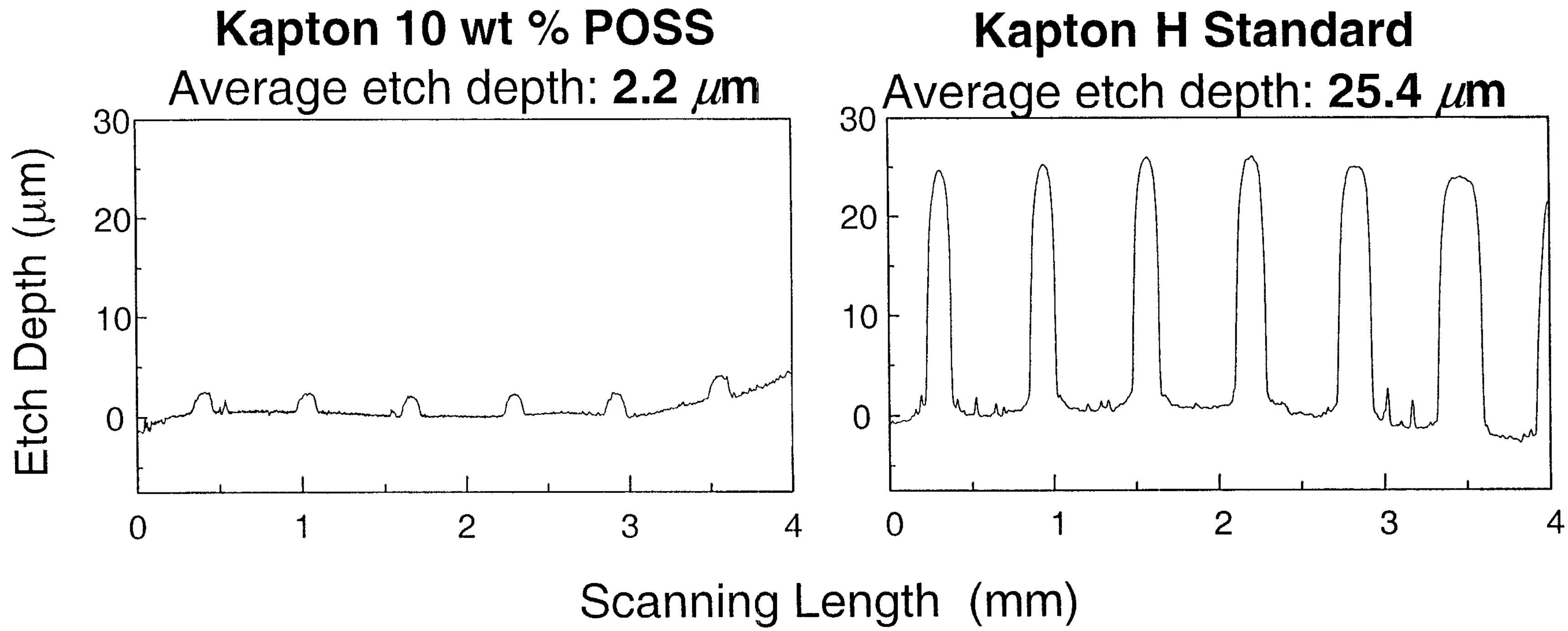
POSS-Insulation Sample



Space Survivable Materials



O atom fluence: 8.47×10^{20} atoms cm^{-2}



Summary

- Nano-sized inorganic clusters (POSS) can be successfully incorporated into a wide variety of different organic polymers.
- These POSS clusters cause increases to the thermal transitions and mechanical properties of the polymers they are copolymerized into.
- Not every POSS is the same and the POSS effect on the properties of analogous polymers shows a dependency on the type of alkyl group on the POSS cluster.
- Rheology of high molecular weight PDMS grafted with small amounts of POSS illustrates a dependence on both the POSS-alkyl-group and POSS shape.
- TEM images of randomly copolymerized polymers illustrate this dependency, as the size of the POSS domains are alkyl-group dependent.

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Prof. Ben Hsiao SUNY
Prof.Frank Feher UCI
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Prof. Tim Minton MSU

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